# APPLICATION OF BANANA STEM AND RICE STRAW DERIVED BIO-FLOCCULANTS FOR TEXTILE WASTEWATER TREATMENT

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# APPLICATION OF BANANA STEM AND RICE STRAW DERIVED BIO-FLOCCULANTS FOR TEXTILE WASTEWATER TREATMENT

**By**

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| AG | Absolute germination |
| ANOVA | Analysis of variance |
| APHA | American Public Health Association |
| ATR | Attenuated Total Reflectance |
| BOD5 | Five-day biochemical oxygen demand |
| BP | Banana pseudo-stem |
| CCD | Central composite design |
| COD | Chemical oxygen demand |
| CD | Charge density |
| DO | Dissolved oxygen |
| GI | Germination index |
| ECH/DMA | Epichlorohydrin and dimethylamine |
| $FeCl_3$ | Ferric/ Iron chloride |
| $FeCl_3P$ | Ferric/ Iron chloride with pectin |
| $FeCl_3PAM$ | Ferric/ Iron chloride with polyacrylamide |
| FTIR | Fourier transform infrared |
| IPA | Isopropyl alcohol |
| ISO | International Organization for Standardization |
| $LC_{50}$ | Lethal concentration |
| LiP | Lignin peroxidases |
| MnP | Manganese dependent peroxidases |

| | |
|---|---|
| MW | Molecular weight |
| OECD | Organisation for Economic Co-operation and Development |
| P | Pectin (extracted bio-flocculant) |
| PAM | Polyacrylamide (synthetic flocculant) |
| PCE | Tetrachloroethylene |
| PDADMAC | polydiallyldimethyl-ammonium chloride |
| polyDADMAC | Poly(diallyldimethyl ammonium chloride) |
| PEO | Poly(ethylene oxide) |
| PSSA | Poly(styrene sulfonic acid) |
| RS | Rice straw |
| RSM | Response surface methodology |
| RY4 | Reactive yellow 4 |
| SPSS | Statistical Package for the Social Science |
| SS | Suspended solid |
| TCE | Trichloroethylene |
| USEPA | United States Environmental Protection Agency |
| WW | Wastewater |

# LIST OF SYMBOLS

| | |
|---|---|
| h | Hour |
| k | Factors/ number of independent variables |
| $W_0$ | Dried product weight after freeze dried |
| W | Dried raw material weight |
| min | Minute |
| rpm | Rotation per minute |
| $C_i$ | Initial colour concentration |
| $C_f$ | Final colour concentration |
| PtCo | Platinum cobalt |
| $N_{germ}$ | Average number of germinated seeds |
| $N_{seed}$ | Total number of seeds |
| $N_{cont}$ | Average number of germinated control seeds |
| $RL_{germ}$ | Average root length of germinated seed |
| $RL_{cont}$ | Average root length of germinated seed |
| y | Response |
| $\xi_i$ | Natural variable |
| $x_i$ | Coded variables |

**APLIKASI BATANG PISANG DAN JERAMI PADI DARIPADA PEMBUKU–BIO BAGI RAWATAN AIR SISA TEKSTIL**

## ABSTRAK

Kajian ini melibatkan tiga peringkat yang berbeza iaitu pembuku-bio yang diekstrak daripada batang pisang dan jerami padi, rawatan efluen terawat air sisa tekstil menggunakan menggunakan ekstrak pembuku-bio dan ujian toksik keatas enapcemar yang terhasil selepas proses pengentalan dan pemberbukuan. Pembuku-bio yang diekstrak daripada batang pisang menggunakan proses ekstrak asid panas didapati lebih tinggi hasilnya iaitu 32.8% sementara hanya 16.2% daripada jerami padi yang berjaya dikumpul daripada berat asal masing-masing (10g). Seterusnya, pembuku-bio dianalisa menggunakan spektoskopi FTIR untuk mengenal pasti kehadiran kumpulan berfungsi yang membantu dalam proses pemberbukuan. Kumpulan hidroksil dan karboksil telah dikenalpasti hadir di dalam analisis FTIR. Efluen terawat air sisa tekstil di analisa bagi pengurangan warna dan keperluan oksigen kimia (COD) menggunakan ujian kelalang oleh pengental ($FeCl_3$) dan pemberbukuan ( P dan PAM). Proses pengentalan dan pemberbukuan dijalankan dengan menggunakan kaedah rekaan sambutan (RSM) dengan rekabentuk ujikaji gabungan pusat bagi melihat keupayaan diantara ($FeCl_3$ dan P) dan ($FeCl_3$ dan PAM) pada keadaan yang optimum dengan pelbagai pembolehubah seperti pH, dos pengental dan dos pemberbukuan. Rawatan menggunakan $FeCl_3$ dan PAM menunjukkan penyingkiran warna yang paling tinggi iaitu 95% (31 pt. co) dan 92.0 % (42 mg/ L) pengurangan COD pada pH sekitar 5.4, 375 mg/ L bahan pengental dan 28 mg/ L bahan pemberbukuan. Manakala rawatan menggunakan $FeCl_3$ dan P berupaya menyingkirkan warna dalam lingkungan 83.0 % (104 pt. co) dan 76.0 % (127 mg/ L) pengurangan kepekatan COD pada pH 7.2, dos pengental 353.0 mg/ L, dan dos

pemberbukuan 30.9 mg/L. Akhir sekali, sisa enapcemar yang terhasil daripada proses itu, di analisa untuk ujian ketoksikan menggunakan benih *Lactuca sativa.* Berdasarkan ujian percambahan bijih benih, enapcemar yang terhasil selepas proses rawatan menggunakan $FeCl_3P$ menunjukkan indeks toksik yang lebih rendah ($LC_{50}$: 55) berbanding PAM ($LC_{50}$: 19). Kesimpulannya, penggunaan pembuku-bio dalam rawatan pengurangan warna dan kepekatan COD daripada efluen terawat air sisa tekstil telah berjaya dirawat. Tambahan lagi, enapcemar yang terhasil juga menunjukkan kesan yang positif dengan kadar toksik yang rendah.

**APPLICATION OF BANANA STEM AND RICE STRAW DERIVED BIO-FLOCCULANTS FOR TEXTILE WASTEWATER TREATMENT**


## ABSTRACT

This study involve three different stages which are extraction of bio-flocculant (P) from banana pseudo-stem and rice straw, treatment of textile wastewater treated effluent using extracted bio-flocculant and phytotoxicity test on the sludge produced after coagulation and flocculation process. The bio-flocculant extracted from banana pseudo-stem using hot acid extraction process was found to be higher in yield at 32.8 % while only 16.2% from rice straw was manage to collect from the dry weight 10 g respectively. Later the bio-flocculant was analysing using Fourier Transform Infrared Spectroscopy (FTIR) to detect the existence of functional group which helps in the flocculation process. Hydroxyl and carboxyl group was detected from the FTIR analysis. The textile wastewater treated effluent was analysed for colour and COD reduction by coagulation ($FeCl_3$) and flocculation (P and PAM) using a standard jar test apparatus. The coagulation and flocculation process was run using Response Surface Design – Central Composite Design in order to see the efficiency between ($FeCl_3$ and P) and ($FeCl_3$and PAM) at the optimum condition with varied parameters such as pH, coagulant dose and flocculant dose. Treatment by $FeCl_3$ and PAM shows the highest colour removal with 95% (31 pt. co) and 92.0 % (42 mg/ L) COD reduction at condition pH around 5.4, 375 mg/ L of coagulant and 28 mg/ L of flocculant dose. While the treatment with $FeCl_3$ and P was able to remove the colour around 83.0 % (104 mg/ L) and 76.0 % (127 mg/ L) of COD reduction at treatment conditions of pH 7.2, coagulant dose 353.0 mg/ L, and flocculant dose 30.9 mg/L. Finally, the sludge residue from the process was analysed for phytotoxicity test using *Lactuca sativa* seeds. Based on the seed germination test, the sludge produce after the process using bio-flocculant showed less toxicity index ($LC_{50}$: 55) rather than PAM ($LC_{50}$: 19). In conclusion, the used of bio-flocculant was a success in order to remove colour and COD of textile wastewater treated effluent. Furthermore, the sludge produced also show a positive effect whilst is at low toxicity index.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Introduction

Generation of municipal solid waste in Malaysia has increased more than 91% within a decade. United States Environmental Protection Agency (USEPA) reported that the organic material has always been the biggest contributor to the municipal solid waste. In 2012, Americans produced about 251 million tons of garbage, from which 87 million tons were recycled and composted, which is equivalent to 34.5 % recycling rate. Garbage should not only be reduced by recycling the trash but also by minimizing the waste generated globally. Likewise, agricultural waste production too has the potential to be recycled and produce new material.

In conjunction, banana pseudostem and rice straw are agricultural waste that have the capability to treat effluent from wastewater by acting as bioflocculating agent. Annually, about 17 million tons of bananas are produced worldwide whilst global paddy production is more than 700 million tons (FAO, 2013). It has been estimated that a few tons per hectare of banana pseudo-stem are produced every year (Cordeiro, Belgacem, Torres & Moura, 2004). Waste generated from the banana plantation was disposed on land and the effluent flows into water bodies, which result in serious ecological hazard. Similarly, a report by the International Rice Research Institute (IRRI) stated that in 2008 approximately 620 million tons of rice straw were produced in Asia alone. These agro wastes are disposed off in various ways and have been reported to be increasing every year. Moreover, open- field burning is practised at some of the paddy fields after the harvesting season, which directly degrade the quality of the atmosphere and releases a great amount of carbon which results in increase in global temperature and ultimately causes climate change. Thus, it can be concluded that inefficient solid waste disposal methods will create series of problems, namely air and water resource pollution, accident hazard, increase of rodents and insect vector disease which leads to serious risk towards the communities (Essien et al., 2005).

## 1.2 Textile wastewater

Textile dyes can be divided into chromophores and auxochromes that are responsible for colourization and enhancing the affinity of dyes towards the fabric (Gupta et al., 2009). It can be classified as cationic, anionic and nonionic dyes. Most of the dyes used in the textile industries are disperse, reactive, acid, basic, and direct dyes which usually have azo derivatives in their structure. This type of derivaties cannot be eliminated completely with only one treatment system. Cationic dyes or basic dyes are known to carry positive charge in their molecule providing high colour intensity and brilliance. Functionality of cationic dyes can be found mainly in cationic azo dyes, methane dyes, anthraquinone, di- and tri-arylcarbenium, phtalocyanine, polycarbocyclic and solvent dyes (Salleh et al., 2011). Crystal violet, methylene blue, basic blue, basic red and malachite green are widely used in dye adsorption studies. By contrast, anionic dyes depend on negative charge that includes direct, acid and reactive dyes. Various type of anionic dyes such as reactive brilliant red, acid turquoise blue, methyl orange, reactive yellow 4 (RY4) are used in the industries. Generally a combination of two or three treatments is needed to reach effluent quality below the standard limit stated in Environmental Quality Act 1974 (Riera-Torres et al., 2010).

## 1.3 Textile wastewater treatment

Industrial developments have been growing over the years and it has generated tons of environmental problems to our water resources. Several of the highest pollution contributors are from various industries such as textile, soap, plastic, painting, inks, paper and pulp industries, which are known for using complex chemicals in their processes. Textile industries release high amount of colour, BOD, COD, temperature, pH, turbidity and heavy metals from their processes (Verma et al., 2012). Wastewater from textile industries especially from dyeing process must be treated before being discharged due to the toxicity level in the wastewater.

Industrial wastewater can be treated using physical, chemical and biological method. Adsorption method has been an effective and most adopted physical method for treating dye wastewaters. Furthermore, activated carbon is a well-known adsorbent, however it needs to be reviewed due to its non-renewable properties and expensive operational cost. Similarly, ion exchange process is also considered as costly but is incapable of treating wide ranges of dyes (Ali et al., 2004).

Previous studies showed the potential of biological treatment as an alternative treatment to remove synthetic dyes from industrial effluents (Binupriya et al., 2010, Chen et al., 2003 and Mohan et al., 2002). Numerous approaches in chemical treatment, such as coagulation/flocculation, chemical oxidation, ozonation, sonolysis, has been investigated by previous researchers. Each process has its own benefit and drawbacks. Although coagulation/flocculation and oxidation is efficient in colour removal, it produces sludge after the treatment, which needs to be disposed off. Martins et al., (2006) stated that ozonation of pararosaniline solution is more efficient than sonolysis treatment. On the contrary, the end product of ozonation generates bromate; known for its carcinogenic properties.

Among the processes, coagulation has been explored widely for colour and COD removal, especially for wastewaters comprising dissolvable dyes that result in high chemical concentration and large volume of sludge. Coagulation is mainly known as a mechanism in destabilizing a colloidal suspension to produce floc for subsequent solids-separation process (water supply and pollution control). Aluminium and iron salt is commonly used in the industries, as it is scientifically proven to remove colour. In addition, there are organic coagulant such as chitosan, moringa oleifera seeds and grape seeds (Jeon et al., 2009) meanwhile aluminium sulphate (alum), ferrous sulphate ($FeSO_4$), and ferric chloride ($FeCl_3$) are frequently used as inorganic coagulant.

Generally, addition of flocculant after the coagulation process aids in binding and linking the particles during collision, thereby bridging the particles together in form of particle-polymer-particle. Flocculant can be divided into two groups; inorganic or organic flocculant. Inorganic flocculant is unfavorable since it is pH sensitive, required in large amount and applicable only to a few disperse systems (Renault et al., 2009). Thus, organic flocculant has been investigated owing to its numerous advantages. At present, natural polymers like pectin has been a resurgence of interest in water treatment as it is biodegradable, renewable resource and not hazardous to the environment. Bio-flocculant can be extracted from any kind of plant and fruit wastes that is abundantly available as byproduct from the agriculture industries. These biopolymers have been extensively studied from different kind of plant such as citrus peel (Ho et al., 2010), sugar beet (Oosterveld et al., 2000), apple pomace (Min et al., 2011), and banana peel (Qiu et al., 2010).

The treatment of dye wastewater using bio-flocculant is essential to develop cleaner technologies, because synthetic flocculant creates non-biodegradable by-product and are based on non-renewable resources such as petrochemicals, whereby the operational production cost is high (Sharma et al., 2007). Furthermore, their residual monomers and other reactants formulated in the synthetic flocculant could bring negative impact to human health (Ozacar and Sengil, 2003).

## 1.4 Problem statements

Nowadays, agro wastes are found to be interesting organic material due to the availability value in the market which can be used in wastewater treatment as bio-flocculant. Many researchers studied the effect of pH, temperature, extracted time, salting out time and solvent to solid ratio in order to get the optimal extracting bio-flocculant. However, only three of the parameters seem to influence considerably on the quantity of pectin; which is pH, temperature and extracted time (Yapo et al., 2007). Qiu et al. (2010) reported that the extraction rate of bio-flocculant increases at higher temperature of the extraction process. While Wai et al. (2010) discovered that pH and time is the most significant parameter on the bio-flocculant yield.

Pectin (P), an important functional group in the bio-flocculant, is efficient in the coagulation and flocculation process. Bio-flocculants with a huge number of carboxyl group (COOH) proved to be the best flocculant since it is able to supply more effective sites for ferric cations to form the bridge (Piriyaprasath and

Sriamornsak, 2011). Ho et al., (2010) stated that the electrolyte group can be exposed from the longer chain of bio-flocculant. The functional group of carboxyl and hydroxyl with the negative charges are able to stretch out the bio-flocculant chain due to the electrostatic repulsion (Yokoi et al., 2002).

Moreover, textile wastewater treatment plant require large amount of coagulant in order to get the highest removal. Studies by Piriyaprasath and Sriamornsak (2011) revealed that the good flocculating activity was obtained between bio-flocculant and ferric ion. The number of coagulants can be reduced by the addition of bio-flocculant which will reduce the amount of sludge being produced. There are few studies related to the benefit of sludge utilisation such as the potentiality of the generated sludge in agriculture as a soil conditioner (Rosa et al., 2007). Therefore the usage of acrylamide monomers in the polyacrlamide (PAM) attributes to hazardous sludge generated that affects the potentiality of the sludge as soil enhancer.

## 1.5 Objectives

- To determine bio-flocculant yield from banana pseudostem and rice straw at various extraction condition (pH, temperature and time).
- To determine the characteristic of bio-flocculant from banana pseudostem and rice straw in term of functional group by using Fourier Transform Infrared Spectroscopy (FTIR).
- To determine the treatment efficiency of textile wastewater treated effluent by using $FeCl_3$ as coagulant while P and PAM as flocculant through coagulation and flocculation process.
- To evaluate the phytotoxicity of sludge residue from the coagulation and flocculation process using individual coagulants ($FeCl_3$) and flocculant (P and PAM).

## 1.6 Overall flow chart of the experiment

This study includes various steps starting with bio-flocculant extraction, FTIR analysis, coagulation- flocculation process and phytotoxicity of the sludge. The overall experimental procedure of the study is shown in Figure 1.1.

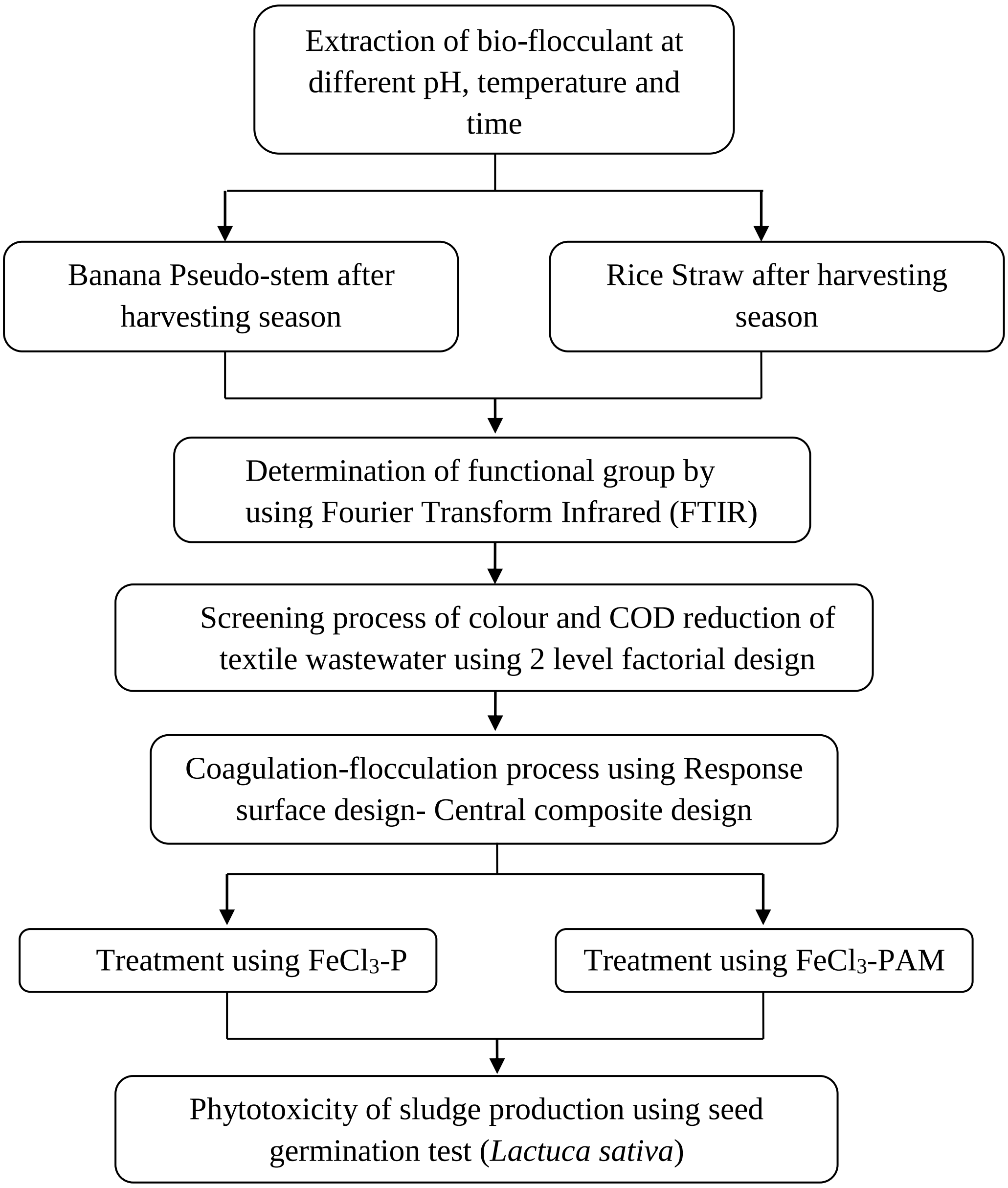


Figure 1.1 Flow chart of the study.

## 1.7 Significance of the study

This research focused on the treatment of the treated effluent from textile wastewater since the number of parameter did not meet the standard limit prescribed by Environmental Quality Act 1974 (Act 127), Regulations, Rules & Orders, 2012. The treatment by coagulation and flocculation using hydrolysing metallic salt ($FeCl_3$) with extracted bio-flocculant and PAM was conducted as comparison.

The findings revealed that the negative impact of using PAM on the aquatic lives via phytotoxicity test compared to extracted bio-flocculant which was more environmental friendly. The possibility of the sludge residue to be used as a soil conditioner in agriculture area was mention by Rosa et al. (2007).

## 1.8 Scope of the study

Coagulation/flocculation can be affected due to many factors other than pH, coagulant dose, and flocculant dose. The factors that are not explored in this study are temperature, settling time, stirring speed and time, which were fixed at certain values. Apart from the constant factors, the study focused more on the lab scale reactor under the same conditions. The reading values of the parameter from the textile wastewater can be inconsistent throughout the experiment. Therefore, the replication of the experiment is counted. The findings of this research are only applicable to the textile wastewater treated effluent with the same condition.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Coagulants: sources and challenges

Hydrolizing metal salt has been widely used in coagulation-flocculation treatment. Existing studies in coagulation and flocculation process used several types of salts (aluminium sulphate, ferric sulphate and ferric chloride) as coagulant in various type of wastewater treatment. At the right concentration, these coagulants act effectively with negative colloids. The reactions will lead to destabilisation and coagulation of the colloids as many of hydrolyzing metal salt is cationic. If the excess coagulant is added, it may affect the efficiency by reversing the charge and restabilize the colloids (Zhao et al., 2010 and Liu et al., 2013).

Researchers have reported concern on Alzheimer's disease from the residual aluminium ions. Moreover, the presence of aluminium was suspected to be carcinogenic and mutagenic. Due to non-biodegradability of synthetic polymers, the remaining of sludge after coagulation-flocculation process has limited potential for recycling (Anastasakis et al., 2009). Given the possible threat, there is important need to control aluminium residue to be below a certain level or to be replaced with different kind of coagulant. In term of health risk, ferric chloride creates lesser concerns compared to conventional aluminium. Furthermore, it is applicable in wide ranges of temperature and pH (Shi et al., 2004).

Other type of coagulant can be extracted via natural based sources which occur to be a viable alternatives for the wastewater treatment. Studies on this biodegradable material such as chitosan, horseradish or drumstick tree (*Moringa* *oleifira*), nirmali seeds (*Strychnos potatorum*), cactus and many kind of natural coagulants which are derived from plant, animal or even bacteria. Usually, it is derived as polysacharide and protein (Renault et al., 2009).

Similar to other coagulants, it can be either anionic, cationic or nonionic polyelectrolytes (Yin, 2010). The presence of hydroxyl groups along chains of galactan and galactomannan allow optimal adsorption sites, even with weak connection. It can be surmised that bridging effect of biopolymeric coagulants will bring advantage to defeat the flaws. In this case, mechanism between adsorption and interparticle bridging; and adsorption and charge neutralization are related with biopolymeric coagulant (Duan and Gregory, 2003).

## 2.2 Types of flocculant: sources and challenges

The effenciency of coagulation and flocculation process can be enhanced by adding flocculant; which can be either, inorganic or organic flocculant. Many studies have proven the ability of organic flocculant along with the hydrolyzing metal salts to reduce the colour and COD of the wastewater (Zahrim et al., 2010). Organic flocculants can be divided ino two categories: synthetic flocculant and bio-flocculant (natural based).

### 2.2.1 Synthetic flocculant

Synthetic flocculants are broadly characterised as cationic, anionic and non-ionic categories. The cationic groups of synthetic flocculant can be derived by inserting the quaternary ammonium group into the polymer backbone but phosphonium and sulfonium groups in the polymers are used to a small extent (Bolto and Gregory, 2007). For example, cationic polyacrylamides are made by copolymerisation of acrylamide with quaternary ammonium derivatives of acrylamide. There are two types of polymers involved in the anionic synthetic flocculant which are i) polymers with carboxyl and ii) sulfonic acid groups. Such as partial hydrolysis of polyacrylamide, or copolymerisation of anionic polyacrylamides (commonly used) using acrylic acid with acrylamide. Polyacrylamide and its derivative are commonly used as synthetic flocculant. Basically it's a non ionic polymer however it can be different through the addition of monomers into the polymers backbone. Examples of synthetic flocculant are tabulated in table below:

Table 2.1 Types of Synthetic flocculant (Somasundaran, 2006)

| Cationic | Anionic | Non-ionic |
|---|---|---|
| • Poly(diallyldimethyl ammonium chloride) (polyDADMAC)<br>• Polyvinylbenzyl<br>• Polydimethyl aminomethyl polyacrylamide<br>• Trimethyl ammonium chloride | • Poly(acrylic acid)<br>• Poly(styrene sulfonic acid) (PSSA).<br>• Anionic Polymer A110 (Kemira)<br>• Hydrolyzed Polyacrylamides<br>• Polyacrylic acid<br>• Polystyrene sulfonate<br>• Polyacrylates | • Polyacrylamide (PAM)<br>• Poly(ethylene oxide) (PEO) |

The charges polymers make the molecule to extend and uncoil along the molecular chain with regards to charge repulsion, thus providing many binding sites to attach and allow the particles to adsorb through electrostatic. The benefit of using anionic synthetic polymer is the ability to create larger shear-resistant flocs by promoting bridging meanwhile denser and more shear-resistant sludge is produced when using cationic and non-ionic polymer. One of the flaws using synthetic flocculant is that it makes the coagulation/flocculation stage more complex but at the same time enhances the operation and economy when used correctly.

### 2.2.2 Biopolymeric flocculant- bacteria

Studies on microbial based flocculant has attracted the attention on using greener technology for wastewater treatment. Few studies have been made conducted using biological method since it is easier to apply and is less costly for industries. Attempts have been made by Buthelezi (2012) using bioflocculants produced by indigenous bacteria in variety of dyes such as medi-blue, mixed dyes, fawn dye and whale dye. The result of the study showed, fawn dyes are the hardest to be removed followed by mixed dyes, medi-blue and whale dyes. The study found that the optimal temperature range is between 35–45 °C for all dyes tested. A very low removal of fawn dye with only 22.13–28.18% removal was observed for isolates *Pseudomonas plecoglossicida*, *Pseudomonas pseudoalcaligenes* and *Staphylococcus aureus*. Pearce et al (2003) mentioned that the acidic nature of fawn dyes makes it resistant and difficut to remove. Decolourization of dyes depends largely on the type of dye, pH, temperature and flocculant concentration. On the other hand, biosorption using microorganism required a longer time in order to achieve an optimum removal. Biosorbent using *Aspergillus niger* fungus and *Spirogyra* sp. a type of fresh water green algae, with autoclaving process was investigated to increase the removal of reactive dye up to 88% at 18 h contact time (Khalaf et al., 2008). It was noticed that the biosorption capacity increased with time, thus longer period of time is required to decolourize the dyes.

Adsorption is the easiest mechanism involved to absorb the dye onto the biomass. But it is not suitable for long term treatment because the dye will become saturated after it is absorbed at a long period of time thus the dye-adsorbent composition required to be disposed (Pearce et al., 2003). *Sphingomonas* sp. has been reported to degrade various compounds like aliphatic homopolyesters, aliphatic-aromatic copolyesters (Abou-Zeid et al., 2004) and microsytin-RR (Wu et al., 2010). Though this process does not require any toxic chemical and low in cost, it depends on the dyes compound and types of microbial employed in order for the process to be success.

Nevertheless, the complexcity of dyes mixture molecules might not be efficiently removed by the microorganism despite the benefit of the process.

### 2.2.3 Biopolymeric flocculant – agrowaste material

Recently, a study on alternative ways with natural based flocculants, like chitosan, tannin, guar gum, xanthan gum and locust bean gum as biopolymeric focculant was conducted. The advantages of biopolymer are known to be biodegradable, renewable resources and non-toxic for environment (Mukherjee et al., 2014). Additionally using biopolymer can prevent any indirect form of pollutant.

Today there are several naturally derived substances used as polyelectrolytes, most of them being based on a polysaccharide skeleton with anionic properties due to the presence of carboxyl groups. An advantage of natural polyelectrolytes, especially for their use in potable water treatment, is that in general they are virtually toxic free. Complex polysaccharide tannin derivatives have been used extensively in potable, wastewater and industrial effluent treatment applications. In addition the usage of biopolymeric flocculant can help to reduce the amount of aluminium sulphate as coagulant (Ozacar and Sengil, 2003).

The potential of pectin as biopolymeric flocculant in wastewater treatment system had been observed by few studies (Ho et al., 2010, Verma et al., 2012). Generally, pectin is extracted from fruit waste such as apple pomace, citrus peel, banana peel and not many studies on other parts of plants like stem or straw. The complex polysaccharide exists in all kinds of plants' primary cell walls. It holds within linear chains of (1-4)-linked α-D-galacturonic acid residues and partly interrupted by (1,2)-linked side-chains consisting of L-rhamnose residues and different types of sugars at the linear structure. The galacturonic acids place carboxyl groups, with some of them are carboxamide group when reacted with ammonia meanwhile others like methyl esters form naturally (Piriyaprasarth and Sriamornsak, 2011). The benefits of having functional groups for example carboxyl–carboxylate by means of electrostatic force can remove cation in dyes and metal ions (Rakhshaee and Panahandeh, 2011). Besides, the presence of negatively charged group on the galacturonic acids resulted in electrostatic repulsion cause from the stretching chain (Ho et al., 2010).

## 2.3 Textile wastewater treatment

Textile industries frequently uses synthetic dyes  in dyeing process and have been increasing in numbers over the years. Over 100, 000 commercial dyes are used with more than 7 x $10^5$ tons of dyestuff has been annually produced in textile industries throughout the world (Robinson et al., 2001). Generally, almost 50 % of these dyes are lost along with organic and inorganic chemicals and end up in the effluent (Khandegar and Saroha, 2013). The acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B under the Environmental Quality Act 1974 (Act 127), Regulations, Rules & Orders, 2012 are shown in Table 2.2 and Table 2.3.

Table 2.2 Acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B (Environmental Quality Act 1974 (Act 127), Regulations, Rules & Orders, 2012).

| **Parameter** | **Unit** | **Standard** | |
|---|---|---|---|
| | | **A** | **B** |
| (i) Temperature | °C | 40 | 40 |
| (ii) pH Value | - | 6.0-9.0 | 5.5-9.0 |
| (iii) BOD5 at 20°C | mg/L | 20 | 50 |
| (iv) Suspended Solids | mg/L | 50 | 100 |
| (v) Mercury | mg/L | 0.005 | 0.05 |
| (vi) Cadmium | mg/L | 0.01 | 0.02 |
| (vii) Chromium, Hexavalent | mg/L | 0.05 | 0.05 |
| (viii) Chromium, Trivalent | mg/L | 0.20 | 0.10 |
| (ix) Arsenic | mg/L | 0.05 | 0.10 |
| (x) Cyanide | mg/L | 0.05 | 0.10 |
| (xi) Lead | mg/L | 0.10 | 0.5 |
| (xii) Copper | mg/L | 0.20 | 1.0 |
| (xiii) Manganese | mg/L | 0.20 | 1.0 |
| (xiv) Nickel | mg/L | 0.20 | 1.0 |
| (xv) Tin | mg/L | 0.20 | 1.0 |
| (xvi) Zinc | mg/L | 2.0 | 2.0 |
| (xvii) Boron | mg/L | 1.0 | 4.0 |
| (xviii) Iron (Fe) | mg/L | 1.0 | 5.0 |
| (xix) Silver | mg/L | 0.1 | 1.0 |
| (xx) Aluminium | mg/L | 10 | 15 |
| (xxi) Selenium | mg/L | 0.02 | 0.5 |
| (xxii) Barium | mg/L | 1.0 | 2.0 |
| (xxiii) Fluoride | mg/L | 2.0 | 5.0 |
| (xxiv) Formaldehyde | mg/L | 1.0 | 2.0 |
| (xxv) Phenol | mg/L | 0.001 | 1.0 |
| (xxvi) Free Chloride | mg/L | 1.0 | 2.0 |
| (xxvii) Sulphide | mg/L | 0.50 | 0.50 |
| (xxviii) Oil and Grease | mg/L | 1.0 | 10 |
| (xxix) Ammoniacal Nitrogen | mg/L | 10 | 20 |
| (xxx) Color | ADMI* | 100 | 200 |

*ADMI-American Dye Manufacturers Institute

Table 2.3 Acceptable conditions for discharge of industrial effluent containing chemical oxygen demand (COD) for specific trade or industry sector (Environmental Quality Act 1974 (Act 127), Regulations, Rules & Orders, 2012).

| Trade/ Industry | Unit | Standard | |
|---|---|---|---|
| | | A | B |
| (a) Pulp and paper industry | | | |
| (i) Pulp mill | mg/L | 80 | 350 |
| (ii) Paper mill (recycled) | mg/L | 80 | 250 |
| (iii) Pulp and paper mill | mg/L | 80 | 300 |
| (b) Textile industry | mg/L | 80 | 250 |
| (c) Fermentation and distillery industry | mg/L | 400 | 400 |
| (d) Other industries | mg/L | 80 | 200 |

Treatment of textile wastewater can be achieved by using physical, chemical or biological process. In most casses the combination of the process are used to enhance the quality of the water discharge. Advantages and disadvantages of each process has been tabulated in the table below.

Table 2.4 Advantages and disadvantages of physical, chemical and biological process.

| Process | Advantages | Disadvantages | References |
|---|---|---|---|
| ***Physical process*** | | | |
| Ion exchange | Good surface area, effective sorbent | Not effective for all dyes, derived from petroleum based material, sensitive to particle | Crini, 2005 |
| Adsorption | Effective for dye removal | Eco-friendly disposal of spent adsorbents, require pretreatment process and costly for maintenance | Verma et al., 2012 |
| Membrane filtration | able to remove all type of dyes | Require poper pretreatment for SS removal , membrane fouling, expensive | Salleh et al., 2011 |
| Irradiation | Effective in lab scale | Need a lot of $O_2$ | Robinson et la., 2001 |
| ***Chemical process*** | | | |
| Cucurbituril | Good sorption capacity for difference type of dyes | Expensive process | Zille et al., 2005 |
| Chemical coagulation-flocculation | Can remove dyes molecules from dyebath effluent, not by partial decomposition of dyes | Increasing sludge produce | Yin, 2010 |
| Ozonation | Efficient for colour removal | Aldehyde by-product | Khandegar and Saroha, 2013 |
| ***Biological process*** | | | |
| Aerobic | Economically attractive and eco-friendly | Slow process | Ola et al., 2010 |
| Anaerobic | Decolourized azo and water soluble dyes | Breakdown of process produce methane and hydrogen sulfide | Robinson et al., 2001 |

**i) Physical process**

Ion exchange has been used in tertiary treatment process of textile wastewater. It changes the undesireable cation and anion molecule of dyes with hydrogen/sodium ion through the resin. Ion exchange resin is composed of an organic or inorganic molecular structure which consists of different functional groups. Usually synthetic resins polymerizes organic compounds into a 3-dimensional porous structure was used in wastewater treatment. There are two types of ion exchange resins: one is known as cationic, which means there is an exchange of positive ion, whereas the anionic exchanges negative ion. Cation exchange resins consist of acidic groups, like sulphonic groups, while basic functional groups is the functional group attached to an anion exchange resins such as amine group. The degree of ionisation represents the strength of the resin. For example sulphonic acid group make a strong cation exchange resin. However this process is not widely chosen since the exchange resin are not very effectives for various types of dyes (Robinson et al., 2001).

The most common physical treatment used in textile wastewater is adsorption due to the simplicity of operation and not accompanied by formation of sludge. In the past, adsorbent that has been used are quite expensive, though an alternative to use natural adsorbent was investigated due to better performance. Low cost adsorbent can be derived from natural materials, biosorbents, agricultural waste and industrial by-products such as grass, wood and saw dust, fruits peel and etc. The adsorption process involved with gas or liquid solute accumulates on the surface of a liquid or solid (adsorbent), to form a film of the adsorbate (Verma et al., 2012).

Besides that, membrane filtration method is also possible to separate and clarify the dye molecules continuously from the wastewater. This method has does not rely on temperature, and can withstand microbial attack and also insensitive to the chemical environment. But at the end of the treatment, it produces some residues that cause disposal difficulties which contribute to clogging, membrane replacement and also expensive treatment (Salleh et al., 2011). Furthermore, this process is only suitable for effluents with lower concentration of dyes and several studies claim that it is hard to minimize the dissolved solid content.

**ii) Chemical process**

Chemical process is widely used in treatment of textile wastewater due to excellent performance such as fenton oxidation, cucurbituril, and coagulation process. The Fenton oxidation was applied successfully until the discharge meets standard limits set by the government. Ferrous ion and hydrogen peroxide are used in this process to oxidize the favourable molecules. Excessive ferrous ions in the hydrogen peroxide produce hydroxyl radical and hydroxide ion against the organic compound in the acidic condition. Trichloroethylene (TCE) and tetrachloroethylene (PCE) are some examples of the organic compund.

In addition, cucurbituril was discovered in early 19th century in the form of formaldehyde and glycoluril. It is known as “cucurbituril” due to its pumpkin-like shape (Cucubitaceae is the plant family ) and “uril” refers to the monumer compound of urea. The mechanism react from the cucurbituril are the host-guest complexation and hydrophobic interaction. Karcher et al (2001) showed an excellent sorption capacity of cucurbituril towards synthetic reactive dyes or even the actual wastewater. Likewise this process is costly to be applied by the industries.

Coagulation means a process that involves the use of chemical coagulants (inorganic or organic polymer) to remove particles compound in the wastewater. The most widely used coagulants are aluminium sulfate, also called as Alum, and iron sulphate or iron chloride. The addition of cationic charge such as $Al^{3+}$ or $Fe^{3+}$ will neutralize the solution by adsorbing onto the surface of negative charge particles and forme the microfloc particles (Ho et al., 2010). Coagulant with trivalent ion is more efficient than divalent ion due to the numbers of unoccupied charges. However the effenciency of the coagulation can be higher if the addition of coagulant aid or also known as flocculant to aggregates the particles. This process contribute to formation of sludge if bio-based polymer is not included in the treatment.

**iii) Biological process**

The common biological processes are frequently ineffective in treating actual textile wastewater, since dyes molecule are complex structured polymers with low biodegradability (Raghu and Ahmed Basha, 2007). This process requires less chemicals and energy which contribute to minimum cost. However biological process needs a longer time to remove any impurities effectively. Five days retention time is needed for the bacterium to remove the colour of high concentrated methelene blue dyes (1000 mg/ L) whereas 92.99 % of COD reduction (Che Noraini et al., 2012).

A few types of biological process such as aerobic, anaerobic, enzymatic treatment and others are applied in the wastewater treatment. Aerobic process run with the existence of air and utilize the aerobic microorganisms which is known as aerobes to digest organic impurities thus resulting in water, carbon dioxide, and biomass. Unlike the anaerobic process, aerobic is suitable for lower organic impurities with high biodegradability like municipal sewage treatment.

On the other hand, anaerobic process does not use oxygen in the process as anaerobic microorganisms (anaerobes) are used to digest organic impurities as their food. Anaerobic process is applicable for medium to high organic impurities and for wastewater that are easy to biodegrade such as effluent from food factories. Reaction kinetic of anaerobic process was lower as compared to aerobic process. Azo dyes were reportedly reduced by gratuitous bacteria (also called as azo reductases) from anoxic sediments under anaerobic condition that resulted in colourless aromatic amines which cause a threat to animals due to the mutagenic, harmful and carcinogenic content (Robinson et al., 2001).

### 2.3.1 Types of textile dyes

Dyes can be differentiated into anionic dyes, cationic dyes and nonionic dyes. Cationic dyes can be referred to as basic dyes meanwhile anionic dyes or also known as disperse dyes comprise of acid dyes, direct and reactive dyes (Salleh et al., 2011). Cationic dyes rely upon positive charge which produce high visible colour yet it is soluble in water. Anionic dyes carries negative ions and contrast in structure, water-solubilizing and ionic substituents (Salleh et al., 2011). Furthermore, textile industries are known to use various type of dyes such as acid dyes, azoic dyes, basic dyes, direct dyes, disperse dyes, mordant dyes, reactive dyes, solvent dyes, sulfur dyes, and vat dyes. Table 2.5 show the classification of several dyes with the usage and chemical types for each classes.

Table 2.5 Classification of dyes (Hunger, 2007)

| Class Principal | Substrates | Method of application | Chemical types |
|---|---|---|---|
| Disperse | polyester, polyamide, acetate, acrylic and plastics | fine aqueous dispersions often applied by high temperature/ pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed | azo, anthraquinone, styryl, nitro, and benzodifuranone |
| Reactive | cotton, wool, silk, and nylon | reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline) | azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic |
| Vat | cotton, rayon, and wool | water-insoluble dyes solubilised by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized | anthraquinone (including polycyclic quinones) and indigoids |

## 2.4 Coagulation and flocculation process in wastewater treatment

The concern on toxic freewastewater treatment are becoming a challenge for researcher to find a better approach for coagulation-flocculation process. Coagulation commonly involves metal salts consists of combining dissolved organic matter with insoluble particles to form large aggregates. Destabilisations of particles occur in order to form micro-floc. After the addition of flocculants, micro-floc particle will bind on more than one particle and will be removed by sedimentation and filtration.